# REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-98-

*0635*

| 1. AGENCY USE ONLY (Leave blank) | 2. REPORT DATE | 3. REPORT TYPE AND DATES COVERED |
|---|---|---|
| | | FINAL   01 Jun 95 To 31 May 98 |

| 4. TITLE AND SUBTITLE | 5. FUNDING NUMBERS |
|---|---|
| EXTENSIONS OF THE EQUATION-OF-MOTION COUPLED CLUSTER METHOD FOR EXCITED STATES | F49620-95-1-0421 |
| | 61103D |
| **6. AUTHOR(S)** | 3484/YS |
| Steven R. Gwaltney & Dr Rodney J. Bartlett | |

| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) | 8. PERFORMING ORGANIZATION REPORT NUMBER |
|---|---|
| University of Florida<br>PO Box 118435<br>Gainesville FL   32611-8435 | |

| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) | 10. SPONSORING/MONITORING AGENCY REPORT NUMBER |
|---|---|
| AFOSR/NL<br>110 Duncan Ave Room B115<br>Bolling AFB DC   20332-8050<br><br>Dr Michael R. Berman | |

**11. SUPPLEMENTARY NOTES**

| 12a. DISTRIBUTION/AVAILABILITY STATEMENT | 12b. DISTRIBUTION CODE |
|---|---|
| Approved for public release;<br>distribution unlimited. | |

**13. ABSTRACT (Maximum 200 words)**

The Partitioned Equation-of-Motion Coupled-Cluster method (P-EOM-CC)1 for excited states is presented and analytical energies for the method are derived and tested. Also presented are analytical derivatives for the Similarity Transformed Equation-of-MOTION Coupled-Cluster method (STEOM-CC)2. One of the papers that appeared in print was a sTEOM-CCSD study of the excited states of this parent molecule for many biologically and potentially industrially significant compounds. The other paper that was prepared and that appeared in the last year was a study of hydrogen bonding and proton affinity in the first excited state of formaldehyde4. Studies of such properties are common in the electronic ground state of molecules, but studies of these properties in excited states have been extremely rare.

| 14. SUBJECT TERMS | | | 15. NUMBER OF PAGES |
|---|---|---|---|
| | | | 16. PRICE CODE |

| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
| (U) | (U) | (U) | (UL) |

# Final Report for AFOSR AASERT F49620-95-I-0421

(Parent Award F49620-92-J-0141)

## EXTENSIONS OF THE EQUATION-OF-MOTION COUPLED-CLUSTER METHOD FOR EXCITED STATES

Steven R. Gwaltney and Dr. Rodney J. Bartlett, PI

*Quantum Theory Project*
*University of Florida*
*PO Box 118435*
*Gainesville FL 32611-8435*

In the final year of my AFOSR AASERT grant number F49620-95-I-0421, several important milestones were achieved, the most important of which was graduation. I was awarded my Ph.D. in December of 1997. My dissertation is entitled *Coupled-Cluster Based Methods for Excited State Energies and Gradients*. In it, the Partitioned Equation-of-Motion Coupled-Cluster method (P-EOM-CC)[1] for excited states is presented and analytical energies for the method are derived and tested. Also presented are analytical derivatives for the Similarity Transformed Equation-of-Motion Coupled-Cluster method (STEOM-CC).[2] Several example applications are also included.

The last year also saw the publication of one journal article, the submission, and appearance of two articles, the submission of a fourth article, and the preparation of a fifth manuscript. One of the papers that appeared in print was a STEOM-CCSD study of the excited states of free base porphin.[3] This is the most complete and highest quality study to date of the excited states of this parent molecule for many biologically and potentially industrially significant compounds. The assignment for the excited states of free base porphin is still a major area of debate, and this paper serves to help elucidate some of these questions.

The other paper that was prepared and that appeared in the last year was a study of hydrogen bonding and proton affinity in the first excited state of formaldehyde.[4] Studies of such properties are common in the electronic ground state of molecules, but studies of these properties in excited states have been extremely rare.

The manuscript which was submitted but which has not yet appeared in press presents gradients for P-EOM-MBPT(2)—the P-EOM-CC method for excited states applied on top of a MBPT(2) ground state. Without analytical derivatives, it is possible to calculate only the energy of the excited state at a given geometry. Analytical derivatives allow routine calculation of geometrical gradients, which make possible potential energy surface searches for minima and transition states.

One more manuscript has been prepared. It presents formulas for analytical energy derivatives for the STEOM-CCSD method. No implementation is presented; however, this is the most complicated coupled-cluster based method for which analytical derivatives have ever been derived.

In total, seven journal articles came out of the three years of the AFOSR AASERT grant. They are listed below.

1. S. R. Gwaltney, M. Nooijen, and R. J. Bartlett, "Simplified Methods for Equation-of-Motion Coupled-Cluster Excited State Calculations," Chem. Phys. Lett. **248**, 189 (1996).

2. J. D. Watts, S. R. Gwaltney, and R. J. Bartlett, "Coupled-Cluster Calculations of the Excitation Energies of Ethylene, Butadiene, and Cyclopentadiene," **105**, 6979 (1996).

3. R. R. Sadeghi, S. R. Gwaltney, J. L. Krause, R. T. Skodjie, and P. M. Weber, "Structure and Dynamics of the $S_3$ State of $CS_2$," J. Chem. Phys. **107**, 6570 (1997).

4. S. R. Gwaltney and R. J. Bartlett, "Coupled-Cluster Calculations of the Electronic Excitation Spectrum of Free Base Porphin in a Polarized Basis," J. Chem. Phys. **108**, 6790 (1998).

5. J. E. Del Bene, S. R. Gwaltney, and R. J. Bartlett, "Base Properties of $H_2CO$ in the Excited $^1n{\to}\pi^*$ State," J. Phys. Chem. A **102**, 5124 (1998).

6. S. R. Gwaltney and R. J. Bartlett, "Gradients for the Partitioned Equation-of-Motion MBPT(2) Method," J. Chem. Phys. (submitted).

7. S. R. Gwaltney, R. J. Bartlett, and M. Nooijen, "Gradients for the Similarity Transformed Equation-of-Motion Coupled-Cluster Method," (manuscript in preparation).

In addition, I gave eight poster presentations at conferences, including one at the HEDM Contractors' Conference in June of 1997.

Finally, I would like to personally thank the Air Force Office of Scientific Research and the managers of the High Energy Density Matter (HEDM) program. With this generous grant much good science was accomplished. The benefits to me from the grant are obvious, including greatly facilitating the completion of my Ph.D. in Chemistry. However, the Air Force has also benefited. For example, the computational techniques developed under this grant have been used, and continue to be used, to study chemical properties such as possible synthesis routes for high energy density molecules. In addition, these tools can help to better understand the relation between the stability of potential propellants and the electronic excited state energetics and structures of the constituent molecules.

HONORS/AWARDS

Dr. Bartlett is a Fellow of the International Academy of Quantum Molecular Sciences, Fellow, 1991, the American Physical Society, Fellow, 1989, and a Guggenheim Fellow, 1986. He was an NSF Postdoctoral Fellow (1971) and an IBM Predoctoral Fellow (1969). He has recently been awarded a University of Florida Research Foundation Professorship (Three-year award, 1997-2000).

---

[1] S. R. Gwaltney, M. Nooijen, and R. J. Bartlett, Chem. Phys. Lett. **248**, 189 (1996).
[2] M. Nooijen and R. J. Bartlett, J. Chem. Phys. **106**, 6441 (1997).
[3] S. R. Gwaltney and R. J. Bartlett, J. Chem. Phys. **108**, 6790 (1998).
[4] J. E. Del Bene, S. R. Gwaltney, and R. J. Bartlett, J. Phys. Chem. A **102**, 5124 (1998).